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(54) Title: NANOMETER-SIZED MOLECULAR SIEVE CRYSTALS OR AGGLOMERATES AND PROCESSES FOR THEIR PRODUCTION

(57) Abstract

A molecular sieve comprising crystals or agglomerates of average diameter 100 nanometers or less, which molecular sieve has a crystal or agglomerate size distribution such that the variance in the longest dimension is less than 15 % of the average longest dimension, and which is capable of forming a colloidal suspension, may be prepared by producing a boiling aqueous synthesis mixture of a silica source and an organic structure directing agent in the form of a hydroxide in an amount sufficient to cause substantially complete dissolution of the silica source, and crystallising the solution at 120 °C or less. The crystal size may be controlled by selection of an appropriate crystallisation temperature.

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NANOMETER-SIZED MOLECULAR SIEVE CRYSTALS OR AGGLOMERATES AND PROCESSES FOR THEIR PRODUCTION

The present invention relates to a molecular sieve comprising crystals or agglomerates whose average largest dimension is of the order of nanometers, and processes for its production.

Molecular sieves are microporous crystalline materials which find many uses in chemical processes. Zeolites, generally based on crystalline aluminosilicate, are a well known class of molecular sieve. For some purposes, the use of small zeolite crystals or agglomerates of crystals is desirable and the intrinsic quality of the zeolite generally improves as the crystal size is reduced. For commercial purposes it is desirable that the crystal or agglomerate size is substantially uniform and the production of small crystal molecular sieves should be accurate and reproducible with respect to the crystal size. It would also be useful for some purposes if the crystals or agglomerates were sufficiently small and uniform that the molecular sieve was capable of forming a colloidal suspension. The applicants have identified a new form of molecular sieve which solves these problems. The applicants have also identified a controllable way to produce such material.

The production of molecular sieves having small crystals has been described in a number of documents. For example, EP-A-173901 describes the production of ZSM-5

zeolite whose crystals are "below 0.3 μm" in size. However, the specific zeolites whose production is described are made up of "aggregates of crystallites ranging in size from about 0.1 to 0.3 μm".

US-A-4205053 describes a process for preparing zeolites such as ZSM-5 and ZSM-35. The smallest crystals produced have a size of 0.2 to 0.5 microns, or are lamellae or lamellar intergrowths of about 0.1 μm in size.

US-A-3781226 and US-A-3926782 describe the production of zeolites KL and ZSM-5. Although the size of crystals produced (0.005 to 0.1 μm) appears to be such that it would be expected that the crystals would form a stable colloidal suspension, the crystals form agglomerates having a size of 0.1 to 1 μm and these agglomerates do not form a stable colloidal suspension. A stable colloidal suspension is one in which the crystals or agglomerates do not visibly separate out of the suspension when the suspension is left for a prolonged period e.g. left standing for a month.

US-A-4526879 describes the synthesis of a low sodium zeolite ZSM-5 from a mixture containing sources of an alkali metal oxide, an aluminum oxide, a silicon oxide, and a combination of amine, a halide and a mutual solvent. Although the crystals produced are stated to be 0.05 to about 20 microns in diameter it is believed that the crystals produced are, in fact agglomerates. No means of controlling the crystal size or uniformity is disclosed.

The present invention provides a molecular sieve comprising single crystals or agglomerates, the crystals or agglomerates having an average largest dimension of 100 nm or less, which molecular sieve has a crystal or agglomerate size distribution such that the variance in the longest dimension is less than 15% of the average longest dimension, which molecular sieve is capable of forming a colloidal suspension.

The particles forming the molecular sieve of the present invention are crystals or agglomerates and are substantially uniform in size. The variance of the largest dimension of the particles is less than 15%, preferably less than 10%, more preferably less than 8% of the average largest dimension of the particles. The largest dimension of the particles, in the case of spherical particles the diameter and, in the case of rhomboid or similar particles e.g. coffin-shaped crystals, is the length of the particle. The variance may be measured e.g. using information depicted by a scanning electron micrograph of the material.

The present invention relates to any molecular sieve which may be prepared using a source of silica and an organic structure directing agent. Preferred sieves include MFI, MEL or β-type zeolites, e.g. ZSM-5, silicalite 1, silicalite 2 and ZSM-11.

A structure directing agent is a molecule which directs the formation of a given molecular sieve by the so-called "templating effect". The role of organic molecules

in molecular sieve synthesis is discussed in Articles published in the literature, e.g. Lok et al, Zeolites 1983, volume 3, pages 282 to 291 and Moretti et al, Chim. Ind. (Milan) 67, No. 1-2, 21 to 34 (1985). The effect of an organic structure directing agent is that in the production of the crystalline framework the organic compound behaves like a template around which the crystalline framework grows, or which causes the crystallisation to be directed to form a particular crystalline framework.

A number of publications relate to the production of zeolites from synthesis mixtures containing organic structure directing agents. EP-A-173901 describes the production of ZSM-zeolite which is synthesised from a mixture containing silica, soda and alumina sources in an aqueous medium containing a polyol such as ethylene glycol, and trace amounts of tetrapropylammonium. The ingredients are mixed at room temperature and pressure and crystallised at temperatures of around 175°C.

US Patent 4205053 describes a process for producing large, easily filtered crystals comprising crystallising an aqueous solution containing a source of silica, a nitrogenous template and a substantially colorless organic basic nitrogen compound, different from the template, and being a quaternary ammonium compound having not more than three methyl, three ethyl or three propyl substituents, or being an amine.

The present applicants have surprisingly found that the production of a molecular sieve in which the largest dimension of the particles is controlled, reproducible and on average 100 nm or less can be obtained by ensuring that the silica in the synthesis mixture for the sieve is dissolved at the boiling point of the synthesis mixture. Dissolution of the silica can be achieved by the use of sufficient organic structure directing agent.

Thus the present invention provides a process for preparing a molecular sieve comprising single crystals or agglomerates, the crystals or agglomerates having an average largest dimension of 100 mn or less, which process comprises preparing a boiling aqueous synthesis mixture comprising:

(i) a source of silica, and

(ii) an organic structure directing agent in the form of a hydroxide, in an amount sufficient to cause substantially complete dissolution of the silica source in the mixture;

and crystallising the synthesis mixture at 120°C or less.

The silica is preferably introduced into the synthesis mixture in solid form e.g. as silicic acid.

The organic structure directing agent is introduced into the synthesis mixture in the form of a base, specifically in the form of a hydroxide.

The structure directing agent may be, for example, the hydroxide of tetramethylammonium (TMA), tetraethylammonium (TEA), triethylmethylammonium (TEMA), tetrapropylammonium (TPA), tetrabutylammonium (TBA), tetrabutylphosphonium (TBP), trimethylbenzylammonium (TMBA), trimethylcetylammonium (TMCA), trimethylneopentylammonium (TMNA), triphenylbenzylphosphonium (TPBP), bispyrrolidinium (BP), ethylpyridinium (EP), diethylpiperidinium (DEPP) or a substituted azoniabicyclooctane, e.g. methyl or ethyl substituted quinucilidine or 1,4-diazoniabicyclo-(2,2,2)octane.

Preferred structure directing agents are the hydroxides of TMA, TEA, TPA and TBA.

The structure directing agent should be present in the synthesis mixture such that the silica is substantially completely dissolved in the synthesis mixture at the boiling point of the mixture. Typically, this will require a molar ratio of structure directing agent to silica of 0.2 or more. The amount of structure directing agent necessary to dissolve the silica will, of course, depend on the amount of silica used in the synthesis mixture. The required amount of silica is determined by the molecular sieve structure the synthesis mixture is intended to produce on crystallisation. When the process is used to produce a highly siliceous zeolite such as zeolite ß, the molar ratio of structure directing agent to silica can be

e.g. 0.5 or more. The amount of structure directing agent required to dissolve the silica in accordance with this process is generally in excess of that required to achieve a structure directing effect.

The process can be used to prepare any molecular sieve which can be crystallised from a synthesis mixture containing an excess of organic structure directing agent. The molecular sieve may be composed mainly of silica, e.g. a silicalite; it may be an aluminosilicate (zeolite) or the aluminium may be partly or wholly replaced by another material such as boron, iron, vanadium, chromium or gallium. Thus the present process may be used to produce borosilicates, ferrosilicates, vanadosilicates or chromosilicates. Examples of sieves which may be produced by the present process include zeolites of MFI type, a silicalite, an MEL-structure e.g. silicalite-2 or ZSM-11, or zeolite-ß.

The synthesis mixture therefore optionally contains other raw material required for the synthesis of the desired molecular sieve. For example, if an aluminosilicate or borosilicate is to be produced, then the synthesis mixture further contains a source of alumina or boron. Other materials commonly used in the synthesis of molecular sieves may also be present in the synthesis mixture, e.g. a source of alkali or alkaline earth metal such as sodium, potassium or magnesium. Conveniently the sources of alumina, alkali and alkaline earth metals and so on are

introduced into the synthesis mixture in the form of solids, preferably finely divided solids.

The alkalinity of the synthesis mixture may be ensured in terms of the molar ratio OH^-/SiO_2, which is preferably 1 or less, and typically less than 0.8. The measurement of OH^-/SiO_2 should include all alkali species when calculating the value of OH^-; e.g. any alkali species introduced with the alkali metal, and should correct for any acidity (H^+) added to the synthesis mixture e.g. resulting from the addition of aluminium sulphate.

The boiling aqueous synthesis mixture may be produced by adding to water the silica, organic structure directing agent and, if present, any other ingredients. The ingredients may be added simultaneously or sequentially.

The synthesis mixture may be formed at room temperature and then brought to boiling point. In another embodiment the ingredients for the synthesis mixture are added simultaneously or sequentially to boiling water. In another embodiment, one or more of the ingredients may be added to water to form an aqueous solution, which solution is then brought to boiling point and the remaining ingredients are added whilst the solution is at boiling point.

The synthesis mixture after boiling may then be crystallised at a temperature of 120°C or less. It is preferred that the synthesis mixture is cooled to around room temperature before being brought to crystallisation

temperature. This allows the mixture to be corrected at room temperature for water loss resulting from the boiling. The exact composition of the synthesis mixture can then be ascertained accurately. Surprisingly the synthesis solutions prepared such that the silica is substantially completely dissolved are so active towards crystallisation that very low crystallisation temperatures can be used.

The crystal or agglomerate size can be varied by varying the crystallisation temperature. The lower the temperature the smaller the particle size. For zeolites containing a source of alumina, the particle size can further be varied by varying the amount of alumina present. However, the effect of varying the amount of alumina is not consistent from zeolite to zeolite. For example, it appears that increasing the alumina content of a synthesis mixture for an MFI-type zeolite results in an increase in crystal size. On the other hand, increasing the aluminum content of a synthesis mixture for producing a zeolite ß results in a decrease in crystal size. Thus for a particular composition of synthesis mixture, i.e. one containing specified amounts of synthesis ingredients, the particle size can be selected quite accurately by selecting an appropriate crystallisation temperature.

It has also been noticed that the highly siliceous zeolite, zeolite ß, may be produced in accordance with this process using a particularly small amount of alumina e.g.

0.0045 moles Al_2O_3 to 1 mole SiO_2, and a surprisingly low crystallisation temperature e.g. as low as 70°C.

The crystals or agglomerates produced by this process may be used e.g. to seed the production of other zeolites, especially in accordance with the process described in our co-pending application no. 9122498.0.

The following examples illustrate the invention.

EXAMPLE 1: SYNTHESIS OF NANOMETER-SIZED MFI (SILICALITE) CRYSTALS

Preparation of synthesis solution. The weight of each reactant is given in grams and the product number of each reactant is given in brackets after the Manufacturer's/ Supplier's name.

TPA OH solution (20% in water)	406.34	(Fluka 88110)
Silicic acid powder (10.2 wt% H_2O)	87.94	(Baker 0324-5)
NaOH pellets (98.4%)	5.73	(Baker 0402)

The TPA-solution was weighed in a 1 litre glass beaker, the NaOH was added and the solution stirred at room temperature until the NaOH dissolved. Next, the silicic acid was added and the mixture heated to boiling whilst vigorously stirring. Heating was continued until a clear solution was obtained. The solution was cooled to room temperature and the weight loss due to the boiling was corrected with demineralized water.

The molar composition of the synthesis mixture was:

$$0.53\ Na_2O/1.52(TPA)_2O/10\ SiO_2/143\ H_2O$$

The OH^-/SiO_2 molar ratio was 0.41.

Crystallisation:

The synthesis solution was divided into 3 portions which were crystallized at respectively 120°C for 22 hours, 80°C for 25.5 hours and at 60°C for 9 days. The crystallization at 120°C was done in a 1 litre stainless steel autoclave; the other crystallizations were done in 250 ml plastic bottles. The crystals were separated from the motherliquor using a high-speed centrifuge. Upon centrifuging the crystals appeared as a bluish transparent gel-like mass on the bottom of the centrifuge beakers.

To wash the product, the crystals were redispersed in demineralized water using an ultrasonic bath and were subsequently centrifuged. The washing was repeated until the pH of the last wash water was about 10. After the last washing step the crystals were again dispersed in about 100 ml of the demineralized water. After standing for about a week the 80°C and 60°C crystals did not show a tendency to settle down on the bottom of the container, therefore the 80°C and 60°C crystals were considered as "colloidal zeolites". Small portions (~25 grams) of the zeolite suspensions were evaporated to dryness (16 hours at 120°) and the resulting solids were air calcined for 24 hours at 550°C. X-ray diffraction of the products all showed the pattern of silicalite-1. To determine the crystal size by SEM a few microliters of the washed zeolite slurries were diluted with about 0.5 ml of water and about 0.5 ml of

ethanol. Of this mixture a few microliters were evaporated on a SEM specimen-stub.

Crystallization of MFI at 50°C.

An identical synthesis mixture as described above was, after filtration through a 0.45 micron Millipore filter, crystallized at 50°C. After 5 days into heating it was observed that the synthesis solution showed a very faint bluish hue, indicating the formation of the first visible crystals. This in turn indicates that, given the low temperature, the formation of the zeolite is surprisingly fast. Upon further heating at 50°C the hue became more and more dominant. After 14 days into heating the crystallization was stopped. The product was washed and recovered as described above. A small portion of the colloidal slurry was dried and calcined in the same way as described above.

Comparative X-Ray diffractograms of the 120°C and 50°C crystals are given in Figure 1.

SEM micrographs showed that the crystallite size strongly depends on the crystallization temperature. The effect of the crystallization temperature on the crystallite size is shown in Figure 2.

From this graph can be seen that at 50°C the size of the crystals is as small as about 25 nanometers. Comparative 104,000 * SEM micrographs of the 120°C and 50°C crystals are shown in Figure 3.

<u>Crystallization at 50°C followed by crystallization at 100°C:</u>

A small portion (about 10 ml) of the reaction slurry obtained after 14 days into heating at 50°C was aged at 100°C during 16 hours. After this extra aging period it appeared that the opacity of the 100°C treated reaction slurry was increased vs the "50°C-opacity", indicating that the reaction mixture was still active for the formation of new crystallites. SEM micrographs of the 100°C treated reaction mixture surprisingly showed that the size of crystals was about the same as the 50°C crystals, namely about 25 nanometers. This could suggest that the 50°C reaction mixture contained crystal nuclei which were significantly smaller than 25 nanometers. Comparative 104,000 * SEM micrographs of the 50°C and the 50°C/100°C product are shown in Figure 4. The above observations suggest that a "low-temperature" mother liquor can be reused to give nanometer sized crystals by simply heating up the clear centrifuged mother liquor at an elevated temperature (i.e. at a higher temperature than that at which the mother liquor was previously held).

<u>EXAMPLE 2: SYNTHESIS OF NANOMETER SIZED MEL-TYPE ZEOLITE</u>

A synthesis solution with a molar composition of:

$$0.55\ Na_2O/1.26\ (TBA)_2O/10\ SiO_2/150\ H_2O$$

and having, therefore an OH^-/SiO_2 molar ratio of 0.36, was prepared as follows:

Preparation synthesis mixture (weight reactants in grams):

A. Tetrabutylammonium hydroxide (40% in water) 111.24 (Flukka 86881)

B. H_2O 111.05

C. Silicic acid powder (10.2% water) 45.74 (Baker 0324-5)

D. NaOH (98.4%) 3.03 (Baker 0402)

A and B were mixed in a glassbeaker, D was added and the material again mixed until D was dissolved. C was added and the mixture heated to boiling whilst vigorously stirring. The mixture continued to be boiled for about 10 minutes; the resulting solution was cooled to room temperature and the weight loss corrected with demineralized water. After cooling to room temperature the solution was slightly hazy. The solution was transferred into 250 ml plastic beaker and the beaker was placed in a 90°C oilbath. The neck of the beaker was connected with a reflux condenser.

After about 2 days into heating formation of crystals was observed, this was indicated by a change in the appearance of the solution, (whitish hue). After 4.5 days into heating the crystallization was stopped. The product was washed and recovered as described above in Example 1.

X-Ray diffraction showed that the product had the pattern of silicalite-2 (MEL). SEM micrographs showed that

the product consisted of rice-like agglomerates with a size between 100 and 200 nanometers.

The X-Ray diffractogram and a 104,000 * SEM micrograph are given in Figure 5.

The preparation was repeated using the same procedure to prepare a synthesis mixture having the same molar composition, i.e.

$$0.55\ Na_2O/1.26\ (TBA)_2O/10\ SiO_2/150\ H_2O.$$

This synthesis mixture was maintained at 67.5°C for 255 hours. As expected the crystal size of the product was less than that produced using a crystallisation temperature of 90°C. The crystal size was about 50 nm.

EXAMPLE 3: SYNTHESIS OF NANOMETER-SIZED ZEOLITE ß

A synthesis mixture with a molar composition of:

$$2.79\ (TEA)_2O/0.04\ Al_2O_3/10\ SiO_2/76\ H_2O$$

was prepared as follows:

Preparation of synthesis mixture (weight of reactants in grams):

A.	Tetra ethylammonium hydroxide (40% in water)	105.36	(Fluka 86632)
B.	$Al(NO_3)_3\ 9\ H_2O$	1.50	(Baker 0.006)
C.	Silicic acid powder ($10.2\%\ H_2O$)	34.32	(Baker 0324-5)

B was added to A and mixed until a clear solution was obtained. C was added to the mixture of A and B and this was then heated up to boiling with vigorous stirring. Boiling was continued for about 10 minutes, the solution

was then cooled to room temperature and the weight loss due to the boiling was corrected with demineralized water. A slightly opaque solution was obtained.

The synthesis solution was transferred to a 250 ml plastic beaker and the beaker was placed in a 99°C oilbath. The neck of the beaker was connected with a reflux condenser. After 4 days into heating the whole solution was whitish opaque indicating the formation of crystalline material. After 10 days into heating the crystallization was stopped. The product was washed several times with demineralized water until the pH of the last wash water was 10.0. The product was dried overnight at 120°C. X-Ray diffraction showed that the product was excellently crystalline zeolite ß. SEM showed that the product consisted of very uniform spherical crystallites with a size between 200 and 400 nanometers.

In a second synthesis two parameters were varied, namely

- the aluminum content of the synthesis mixture was increased from 0.04 moles/10 moles SiO_2 to 0.06 moles/ 10 moles SiO_2, hence the composition of the synthesis mixture was:

  $2.79\ (TEA)_2O/0.06\ Al_2O_3/10\ SiO_2/76\ H_2O$, and

- the crystallization temperature was decreased from 99°C to 85°C.

The synthesis mixture was prepared with the same ingredients and in the same way as described above.

After 5 days into heating at 85°C the whole solution was whitish opaque indicating that the formation of crystals had started. After 11 days into heating the crystallization was terminated. The product was washed/recovered as described above.

X-Ray diffraction showed that the product was excellently crystalline zeolite ß and according to SEM the crystals had a size of about 90 nanometer. The X-Ray diffractogram and a 104,000 * SEM micrograph are shown in Figure 6.

A third experiment was done to observe what happened if the synthesis solution did not contain added alumina, hence the molar composition of the synthesis solution was:

$$2.79\ (TEA)_2O/10\ SiO_2/76\ H_2O$$

The solution was, like in the first synthesis, aged at 99°C. After 4 days into heating white solids were formed at the bottom of the beaker while the supernatant liquor was transparent. After 10 days into heating the whole solution had turned into a viscous white slurry. X-Ray diffraction showed that the product had the typical pattern of a layered silica and did not contain a trace of zeolite ß.

From these experiments can surprisingly be concluded that:

- the addition of only a small amount of aluminum, e.g. 0.004 moles Al_2O_3/mole SiO_2 the

crystallisation completely shifts from non-ß to ß.

- zeolite ß can crystallize at temperatures such as 85°C, significantly lower than had previously been suggested (T > 100°C).

EXAMPLE 4: CRYSTALLISATION OF ZEOLITE ß AT 70°C

A synthesis mixture was prepared using the following ingredients (weight of reactants in grams):

TEAOH	(40% in water)	105.37	(Fluka 86632)
$Al(NO_3)_3\ 9H_2O$		3.00	(Baker 0.006)
Silicic acid powder (10.2% H_2O)		34.33	(Baker 0324-5)

The Al species was predissolved in the TEA solution at room temperature. Next the SiO_2 was added. The mixture was heated to boiling with vigorous stirring until the silica was dissolved. Boiling was continued for another ten minutes. The solution was cooled to room temperature and the weight loss due to boiling was corrected with water.

The molar composition of the synthesis mixture was:

$$2.79\ (TEA)_2O\ /\ 0.080Al_2O_3\ /\ 10SiO_2\ /\ 76H_2O$$

Crystallisation:

140.13 grams of the synthesis mixture was transferred to a 200 ml flask, which was placed in a room temperature oil bath and the neck of the flask was connected with a condenser. The oil bath was heated within about 30 minutes to 70°C and maintained at that temperature for 25 days.

Observations during heating:

Days 1 to 14 : No change in appearance.

Days 14 to 18: Solution very gradually took on a whitish hue.

Days 18 to 25: Whitish hue slowly turns into a clear whitish haziness. Crystals did not settle on the bottom of the flask.

After 25 days into heating half of the synthesis mixture was removed to recover the product. The recovery was carried out by washing the product three times with 200 ml of water. The product was dried overnight at 105°C.

XRD showed that the product was pure zeolite ß. The XRD and SEM micrographs are shown in Figure 7. The average crystal size was around 50 nanometers.

COMPARATIVE EXAMPLE 1

The process of Example 2 of US-A-3781226 was repeated. According to US-A-3781226 the material produced had the following chemical composition (expressed as mole ratios)

$$1.5\ (TPA_2O):0.86(Na_2O):73.4(SiO_2):Al_2O_3$$

The product was stated to have a crystal size of about 0.04 micron. An SEM micrograph (magnification 10000*) of the material produced by the applicants when this example was repeated is shown in Figure 8. The product comprised agglomerates with a size between 0.3 and 1.5μm. This would not form a stable collodial suspension.

COMPARATIVE EXAMPLE 2

The process of Example 2 of US-A-3926782 was repeated. According to US-A-3926782 the product was 90% ZSM-5 and comprised crystallite agglomerates of 0.1 to 0.3 μm in diameter. Figure 9 shows an SEM micrograph (magnification 10000*) of the product obtained when the applicants repeated this example. It can be seen that the product comprised agglomerates of 0.2 to 1.5μm in size. This would not form a stable collodial suspension.

CLAIMS

1. A molecular sieve comprising single crystals or agglomerates, the crystals or agglomerates having an average largest dimension of 100 nm or less which molecular sieve has a crystal or agglomerate size distribution such that the variance in the longest dimension is less than 15% of the average longest dimension, and is capable of forming a colloidal suspension.

2. A molecular sieve as claimed in claim 1 in which the variance in the longest dimension is less than 10% of the average longest dimension.

3. A molecular sieve as claimed in claim 1 or 2 which is an MFI, MEL or β-type zeolite.

4. A process for preparing a molecular sieve comprising single crystals or agglomerates, the crystals or agglomerates having an average largest dimension of 100 nm or less, which process comprises preparing a boiling aqueous synthesis mixture comprising:

(i) a source of silica, and

(ii) an organic structure directing agent in the form of a hydroxide, in an amount sufficient to cause substantially complete dissolution of the silica source in the mixture;

and crystallising the synthesis mixture at 120°C or less.

5. A process according to claim 4 in which the synthesis mixture comprises ingredients present in amounts sufficient to produce an MFI, MEL or β-type zeolite on crystallisation of the synthesis mixture.

6. A process according to claim 5 in which the silica source is added to the synthesis mixture in the form of a solid.

7. A process according to claim 6 in which the silica source is silicic acid.

8. A process according to any one of claims 4, to 7 in which the molar ratio of the structure directing agent to silica in the synthesis mixture is 0.2 or greater.

9. A process according to any one of claims 4 to 8 in which the synthesis mixture further comprises a source of aluminum, gallium, boron, chromium, iron, vanadium, alkali metal, or alkaline earth metal.

10. A process according to any one of claims 4 to 9 in which the organic structure directing agent is tetramethylammonium hydroxide, tetraethylammonium hydroxide, tetrapropylammonium hydroxide or tetrabutylammonium hydroxide.

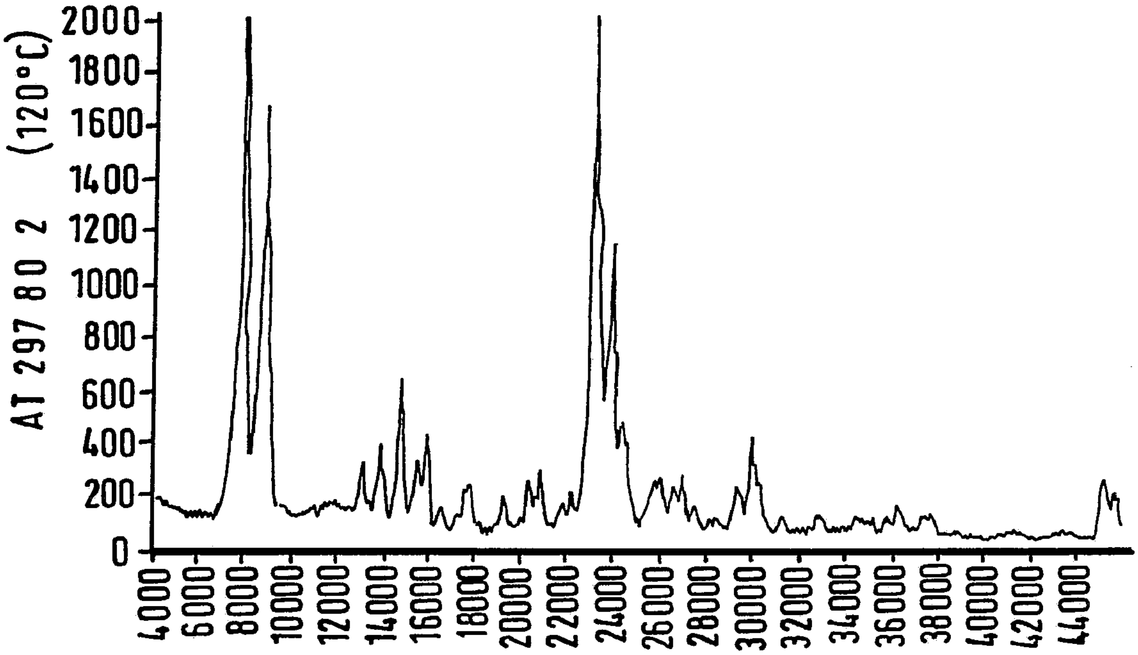
11. A process according to any one of claims 4 to 10 in which the alkalinity of the initial synthesis mixture, expressed as a molar ratio of OH^-/SiO_2, is 1 or less.

12. A colloidal suspension of a molecular sieve as claimed in any one of claims 1 to 3 or as produced according to any one of claims 4 to 11.

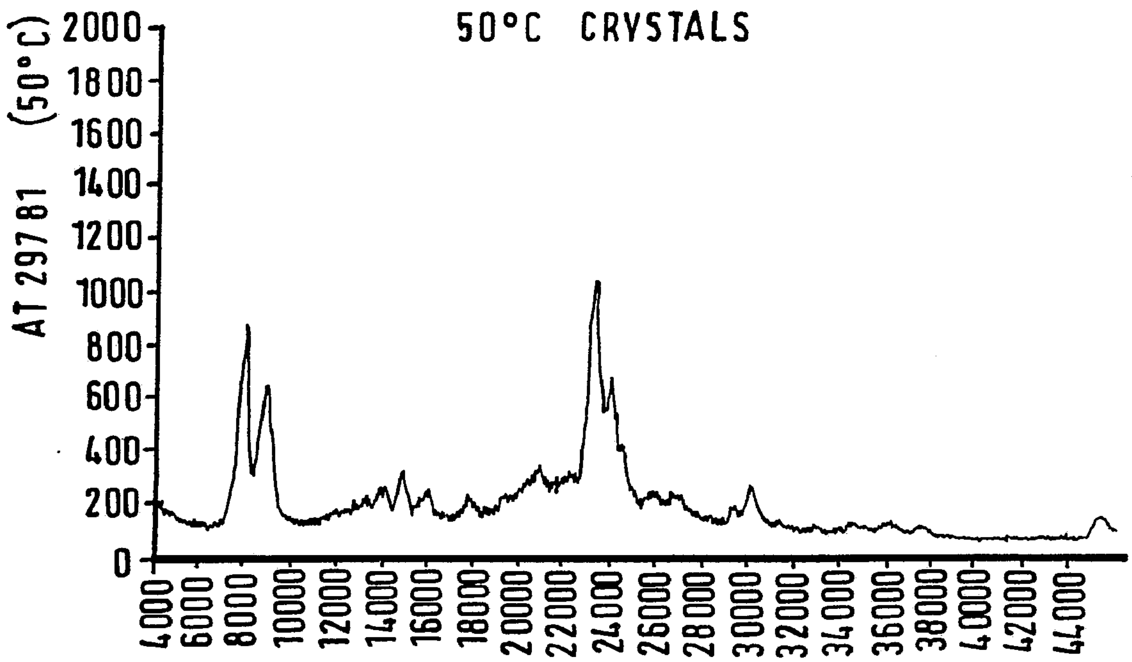
13. Use of a molecular sieve as claimed in any one of claims 1 to 3 or as produced according to any one of claims 4 to 11 or a colloidal suspension as claimed in claim 12 to seed the production of molecular sieve crystals.

FIG.1

120° CRYSTALS



50°C CRYSTALS



SUBSTITUTE SHEET

FIG. 2

EFFECT OF SYNTHESIS TEMP. ON MFI-CRYSTALLITE SIZE

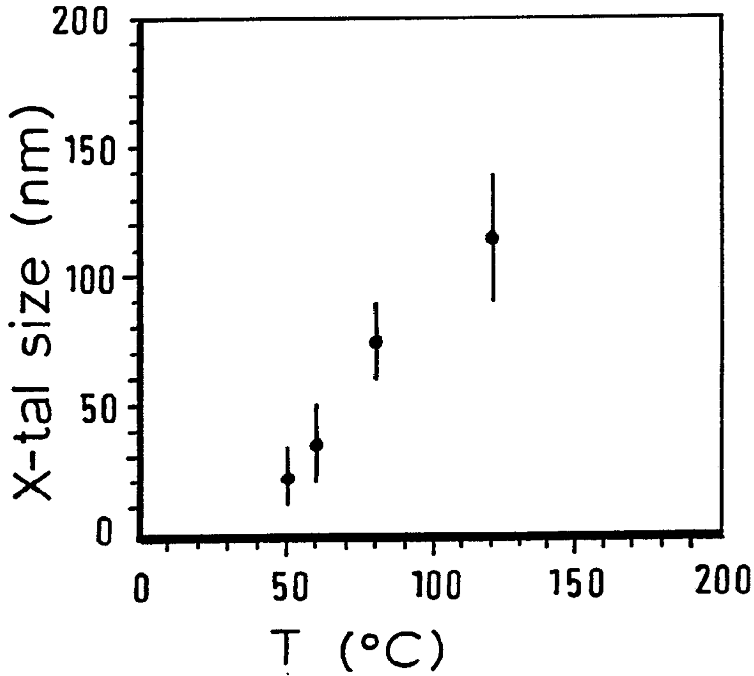
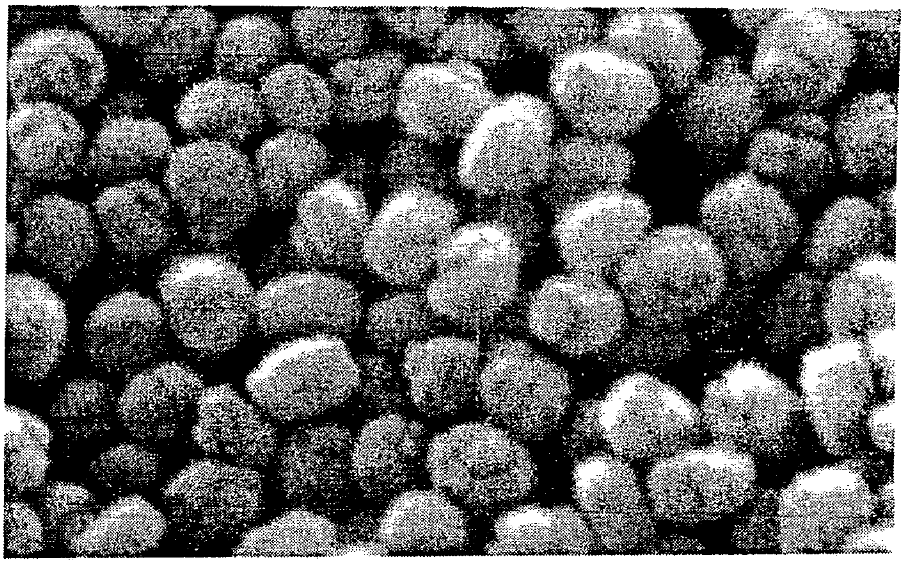


FIG. 3

MAGNIFICATION : 104,000 *

120°C - CRYSTALS



50°C - CRYSTALS

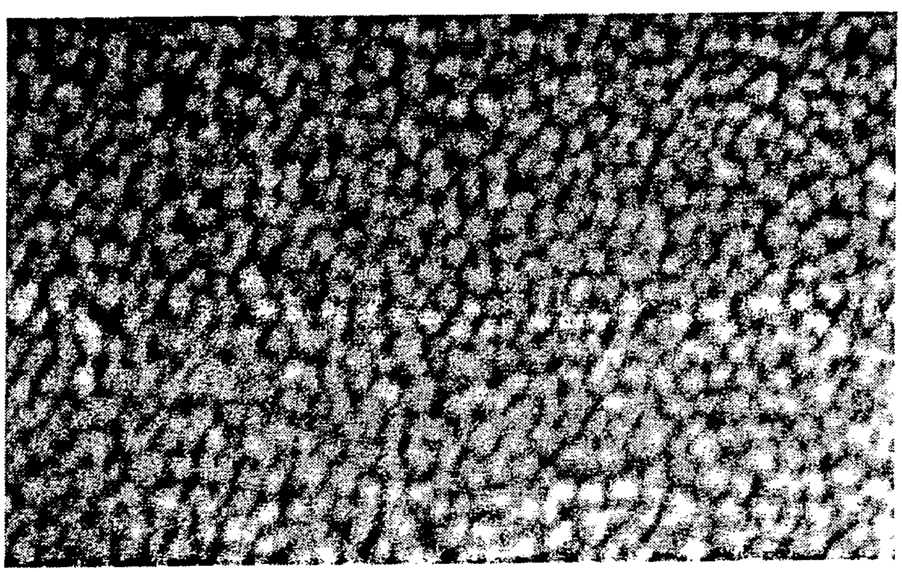
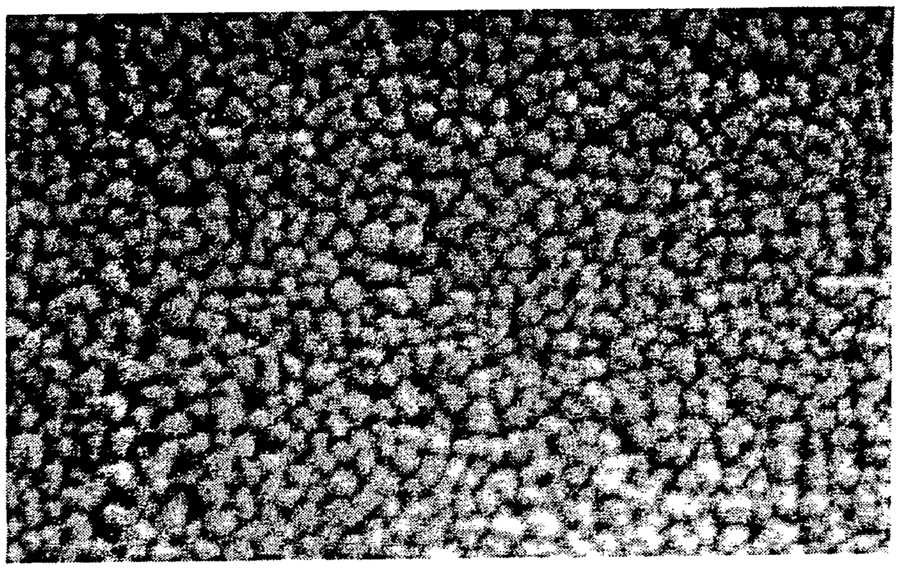


FIG.4

COMPARATIVE 140 000 * SEM MICROGRAPHS

SILLICATE – 1 PRE AGED AT 50°C



SILLICATE -1 PRE AGED
AT 50°C FOLLOWED BY 100°C CRYSTALLISATION

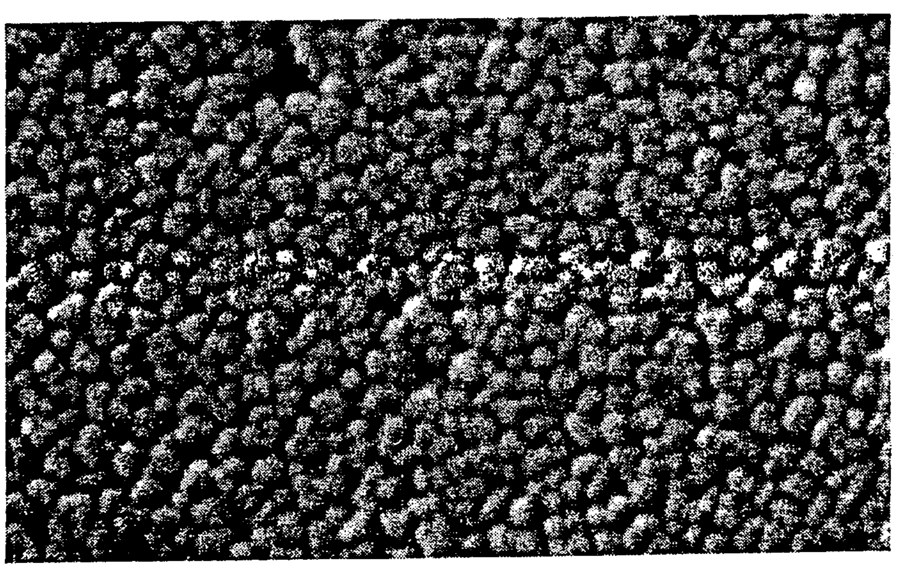
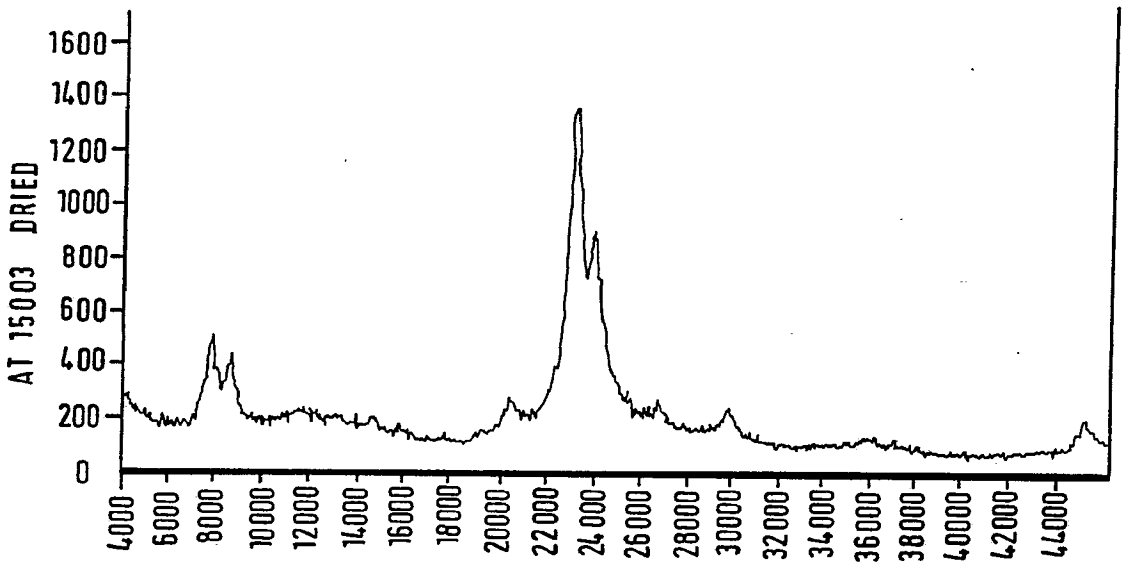
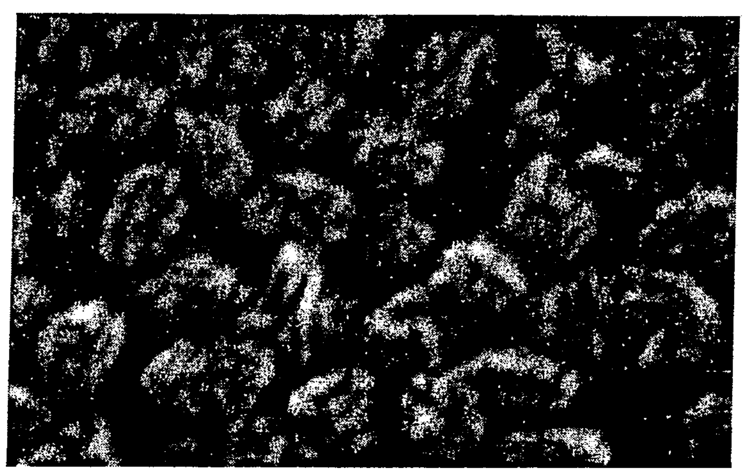


FIG.5

XRD OF PRODUCT DRIED AFTER SYNTHESIS



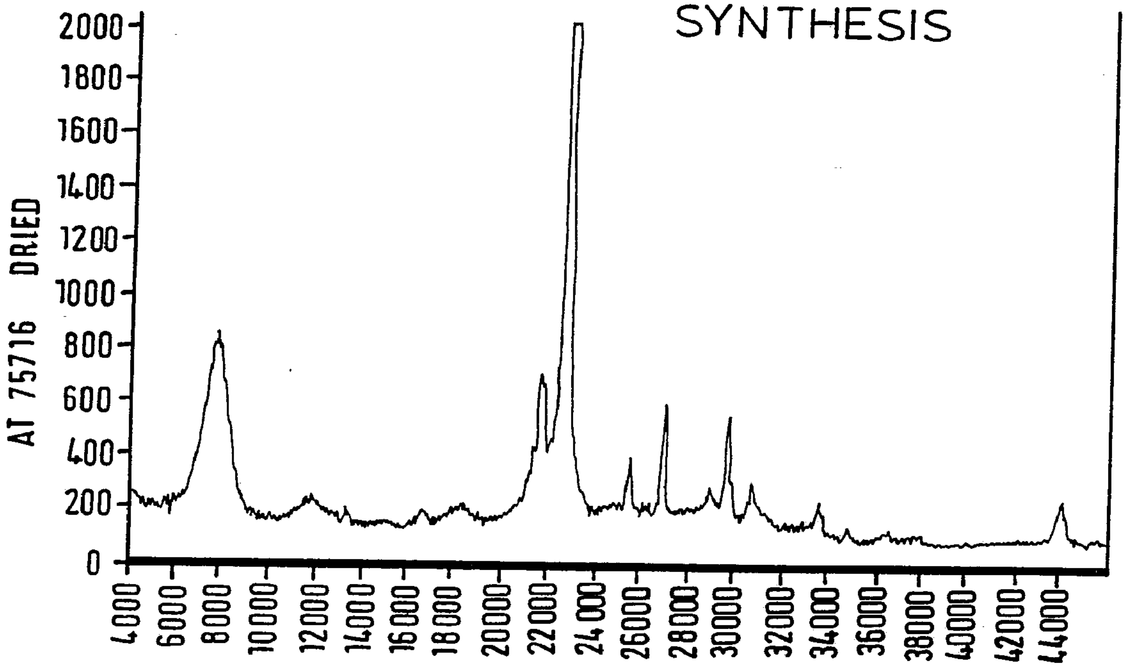
MAGNIFICATION 104,000 *



SUBSTITUTE SHEET

FIG.6

XRD OF PRODUCT DRIED AFTER SYNTHESIS



MAGNIFICATION 104,000 *

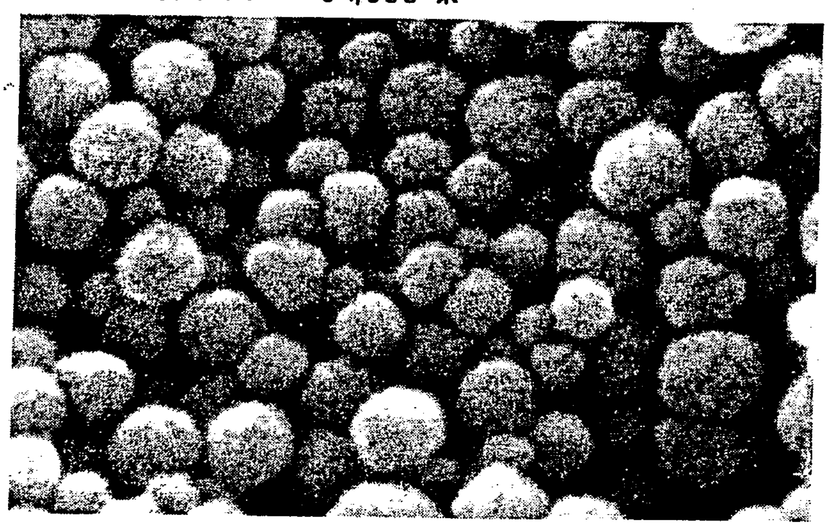


FIG.7

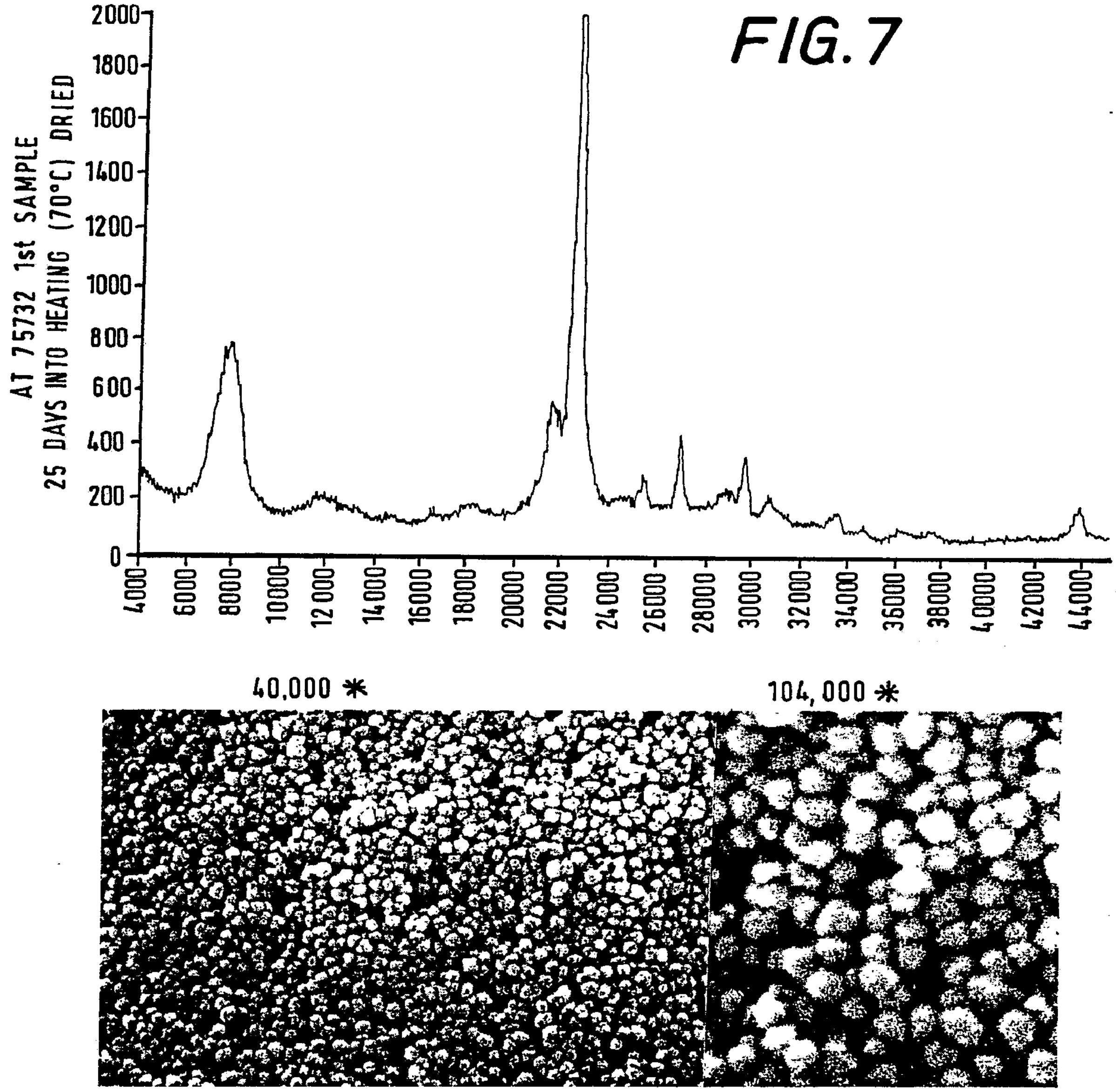
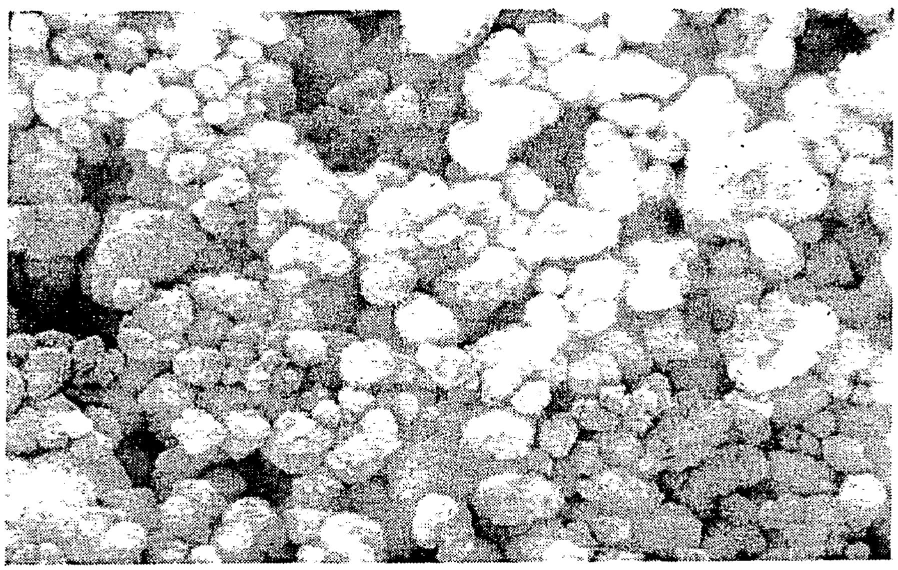

AT 75732 1st SAMPLE
25 DAYS INTO HEATING (70°C) DRIED
2000
1800
1600
1400
1200
1000
800
600
400
200
0
4000
6000
8000
10000
12000
14000
16000
18000
20000
22000
24000
26000
28000
30000
32000
34000
36000
38000
40000
42000
44000
40,000 *
104,000 *

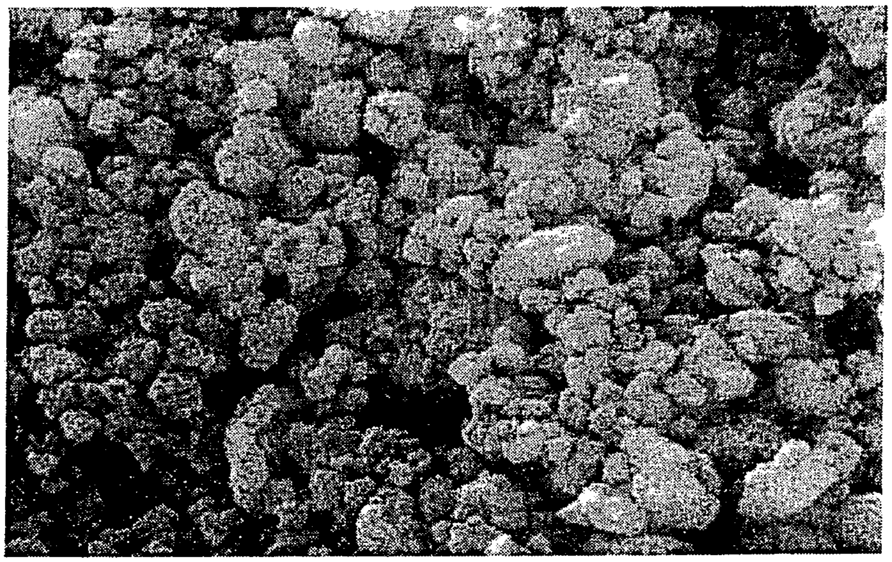
FIG. 8

MICROGRAPH SHOWING AGGLOMERATES WITH SIZES BETWEEN 0·3 AND 1·5 μm



MAGNIFICATION : 10,000 *

FIG.9



MAGNIFICATION : 10,000 *

MICROGRAPH SHOWING AGGLOMERATES WITH A SIZE BETWEEN 0·2 AND 1·5 μm

INTERNATIONAL SEARCH REPORT

International Application No PCT/EP 92/02386

I. CLASSIFICATION OF SUBJECT MATTER (if several classification symbols apply, indicate all)[6]

According to International Patent Classification (IPC) or to both National Classification and IPC

IPC5: C 01 B 33/34, 33/20

II. FIELDS SEARCHED

Minimum Documentation Searched[7]

Classification System	Classification Symbols
IPC5	C 01 B

Documentation Searched other than Minimum Documentation to the Extent that such Documents are Included in Fields Searched[8]

III. DOCUMENTS CONSIDERED TO BE RELEVANT[9]

Category *	Citation of Document,[11] with indication, where appropriate, of the relevant passages[12]	Relevant to Claim No.[13]
A	EP, A1, 0059990 (SHELL INTERNATIONALE RESEARCH MAATSCHAPPIJ B.V.) 15 September 1982, see page 5, line 7 - line 12 --	1-13
A	DE, C2, 3028980 (SHELL INTERNATIONALE RESEARCH MAATSCHAPPIJ B.V.) 14 August 1991, see page 6, line 61 - line 65 -- --------	4-11

* Special categories of cited documents: [10]

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"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)

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"P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

"X" document of particular relevance, the claimed invention cannot be considered novel or cannot be considered to involve an inventive step

"Y" document of particular relevance, the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.

"&" document member of the same patent family

IV. CERTIFICATION

Date of the Actual Completion of the International Search	Date of Mailing of this International Search Report
30th December 1992	20. 01. 93
International Searching Authority	**Signature of Authorized Officer**
EUROPEAN PATENT OFFICE	May Hallne

Form PCT/ISA/210 (second sheet) (January 1985)

ANNEX TO THE INTERNATIONAL SEARCH REPORT ON INTERNATIONAL PATENT APPLICATION NO. PCT/EP 92/02386

SA 65761

This annex lists the patent family members relating to the patent documents cited in the above-mentioned international search report.
The members are as contained in the European Patent Office EDP file on 30/10/92
The European Patent office is in no way liable for theseparticulars which are merely given for the purpose of information.

Patent document cited in search report	Publication date	Patent family member(s)		Publication date
EP-A1- 0059990	15/09/82	AU-B-	548121	21/11/85
		AU-D-	8109282	09/09/82
		CA-A-	1181570	29/01/85
		JP-B-	2044770	05/10/90
		JP-A-	57156321	27/09/82
		NL-A-	8101061	01/10/82
		US-A-	4383981	17/05/83
DE-C2- 3028980	14/08/91	AU-B-	540674	29/11/84
		AU-D-	6091380	05/02/81
		BE-A-	884422	23/01/81
		CA-A-	1144142	05/04/83
		FR-A-B-	2462389	13/02/81
		GB-A-B-	2055357	04/03/81
		JP-B-	1011566	27/02/89
		JP-C-	1529134	15/11/89
		JP-A-	56022623	03/03/81
		NL-A-	7905941	04/02/81
		US-A-	4371628	01/02/83

For more details about this annex : see Official Journal of the European patent Office, No. 12/82

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